

## Pressure-induced transition in the multiferroic $\text{CoCr}_2\text{O}_4$ spinel

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We have explored the high-pressure structural, vibrational, electronic, and magnetic behavior of the multiferroic  $\text{CoCr}_2\text{O}_4$  spinel up to 30 GPa by means of x-ray diffraction, Raman spectroscopy, and density functional theory calculations. Our investigations revealed a reversible tetragonal distortion of the starting cubic structure above 16 GPa. We suggest that the structural modification is mainly driven by magnetic effects induced under pressure. The results obtained are compared with the high-pressure behavior of related spinels.

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### I. INTRODUCTION

The family of  $\text{ACr}_2^{3+}\text{X}_4$  spinels ( $\text{A}^{2+} = \text{Mn-Zn, Cd, Hg}$ ;  $\text{X}^{2-} = \text{O, S, Se}$ ) has recently reattracted significant attention, owing to the discovery of multiferroic properties in several of its members [1–4]. These compounds have been studied extensively over the years due to the intimate coupling between their structural, electronic, and magnetic properties [5–7]. For example, significant magnetoelastic coupling takes place near the magnetic ordering temperatures for these systems, accompanied frequently by structural transitions [6–8]. More recent investigations indicate the close connection between the structure and macroscopic electrical polarization for the multiferroic Cr-based spinels [4,9,10].

Given this strong interrelation between structural, vibrational, magnetic, and electronic degrees of freedom, the variation of the lattice by external pressure provides an appealing method for tuning the physical properties of these materials. Actually, several high-pressure studies reveal structural [11–13], electronic [13,14], and magnetic [13,15] transitions or changes for Cr-based spinels upon compression.

Here we focus on the effect of pressure on the structure, lattice dynamics, and magnetism of the multiferroic  $\text{CoCr}_2\text{O}_4$ . At ambient conditions,  $\text{CoCr}_2\text{O}_4$  crystallizes in the normal spinel structure [space group (SG)  $Fd\bar{3}m$ ,  $Z = 8$ , Fig. 1]. In this phase, the orbitally inactive  $\text{Co}^{2+}$  ( $3d^7:e^4t_2^3$ ) and  $\text{Cr}^{3+}$  ( $3d^3:t_2^3e_g^0$ ) cations occupy tetrahedral and octahedral sites, respectively. Upon lowering temperature,  $\text{CoCr}_2\text{O}_4$  undergoes three successive magnetic transitions [16,17] due to the competing Cr-Cr, Co-Cr, and Co-Co exchange interactions: ferrimagnetic ordering sets in below  $T_C \approx 95$  K, followed by a transition into an incommensurate conical-spiral state at  $T_S \approx 26$  K. Lowering temperature further leads to an incommensurate-to-commensurate transition at  $T_L \approx 14$  K. In addition, spin-induced ferroelectricity has been observed below  $T_S$  [3,18,19], thus making  $\text{CoCr}_2\text{O}_4$  multiferroic; more

recent studies, however, place the coupling between magnetic moments and electric dipoles below  $T_C$  already [20,21]. Quite interestingly,  $\text{CoCr}_2\text{O}_4$  retains its starting cubic symmetry down to 10 K [7,22], even though there has been speculation about a structural modification below  $T_C$  [21].

The available high-pressure investigations on this material have focused on the dependence of the various magnetic ordering temperatures [23–25]. From these studies, it is shown that pressure enhances all of the  $T_C$ ,  $T_L$ , and  $T_S$  at almost similar rates. Since structural data are lacking, however, the microscopic picture for understanding this pressure-induced increase of the magnetic frustration remains incomplete. Here, we report on the effect of pressure on the structural and vibrational properties of  $\text{CoCr}_2\text{O}_4$  up to 30 GPa by means of x-ray diffraction (XRD) and Raman spectroscopy, respectively. Our experimental results are complemented by density functional theory (DFT) calculations of the electronic and magnetic properties of  $\text{CoCr}_2\text{O}_4$  under compression.

### II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Details of the sample synthesis have been reported elsewhere [16]. Pressure was generated with a symmetric diamond anvil cell (DAC), equipped with 300  $\mu\text{m}$  culet diamonds. The ruby luminescence method was employed for pressure calibration [26].

The monochromatic angle-dispersive high-pressure XRD measurements were performed at the 16BM-D beamline of the High Pressure Collaborative Access Team, at the Advanced Photon Source of Argonne National Laboratory. The x-ray beam wavelength was  $\lambda = 0.4246$  Å. The measured XRD diffractograms were processed with the FIT2D software [27]. Refinements were performed using the GSAS + EXPGUI software packages [28,29]. The  $P$ - $V$  data were fitted with a Birch-Murnaghan equation of state [30] (BM EOS). Helium served as a pressure-transmitting medium (PTM).

The high-pressure Raman spectroscopic studies were conducted on single-crystalline  $\text{CoCr}_2\text{O}_4$  samples with a solid-state laser ( $\lambda = 532$  nm) coupled to a single-stage Raman spectrometer (Andor S500i) and a charge-coupled device. The

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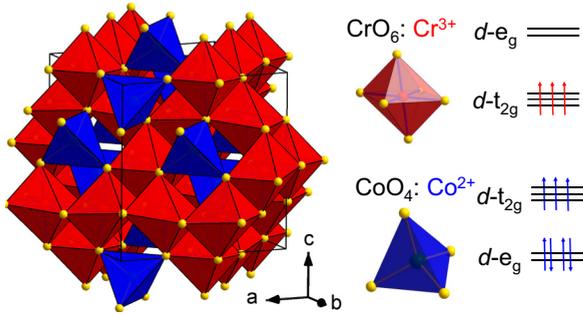


FIG. 1. (Color online) Polyhedral view of the crystal structure of  $\text{CoCr}_2\text{O}_4$  spinel at ambient conditions (SG  $Fd-3m$ ,  $Z = 8$ ). The blue and red polyhedra represent the  $\text{CoO}_4$  tetrahedra and the edge-sharing  $\text{CrO}_6$  octahedra.

size of the laser spot on the sample surface was approximately  $30\ \mu\text{m}$ , whereas the laser power was 3 mW measured outside the DAC. Both helium and a mixture of methanol-ethanol-water 16:3:1 served as PTM in separate runs.

The *ab initio* density functional theory calculations have been performed with the Vienna *ab initio* simulation package [31–34]. Potentials of Co, Cr<sub>p</sub>v, and O using the projector-augmented wave method [35,36] were selected, with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [37,38]. Cr<sub>p</sub>v stands for the Cr potential that includes the semi-core 3p orbital electrons. Because transition metal oxides are correlated materials, the GGA +  $U$  correction scheme was used for the  $d$  orbitals of Co and Cr. The  $U$  values were chosen to be 3.3 for Co and 3.7 for Cr [39,40]. The plane-wave cutoff energy was chosen to be 520 eV to ensure lattice parameter relaxations. During the electronic iterations, Gaussian smearing was used with a  $\sigma$  value as small as 0.1 eV, until the convergence criterion of  $10^{-5}$  eV was reached. During each run, the atomic positions (internal parameters) were allowed to freely relax according to the cell symmetry.

Care was taken to construct the cells with various magnetic configurations. We used the special quasirandom structure (SQS) generation algorithm [41,42] provided in the Alloy Theoretic Automated Toolkit (ATAT) [43,44] to obtain the paramagnetic cubic spinel structure, with a binary spin-up and spin-down construction for the  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  to maintain 0 total magnetic moments for each species, respectively. The  $\Gamma$ -centered  $k$ -point,  $2 \times 2 \times 2$ , mesh was selected. For the ferrimagnetic tetragonal structure, all  $\text{Co}^{2+}$  were given spin-up states, and half of  $\text{Cr}^{3+}$  in the same plane on the  $c$  axis were given spin-up states, the other half spin-down, simulating the experimental configuration [17]. The  $\Gamma$ -centered  $k$ -point,  $3 \times 3 \times 3$ , mesh was selected. The  $c$  axis was allowed to freely relax against  $a$  and  $b$  for each manually set volume. In both magnetic constructions, each magnetic moment was set to be  $3\mu_B$  in magnitude, and their values stayed around  $2.7\mu_B$  ( $\text{Co}^{2+}$ ) and  $2.9\mu_B$  ( $\text{Cr}^{3+}$ ) throughout the electronic iterations without sign change.

To obtain the equilibrium lattice constants, we picked six volume values covering the equilibrium volume and fitted the total energy to a BM EOS [30]. We then obtained the pressure values of each volume from the  $P(V)$  formulation of the same EOS. The total densities of states (TDOSs) were

calculated with  $k$ -point meshes of twice the mesh density stated above in each reciprocal vector direction. Bader charge transfer analysis [45–47] was done with the implementation following the theoretical guidelines [48,49] as described elsewhere [50–53]. The fast Fourier transform grid for charges was set at  $300 \times 300 \times 300$ .

### III. RESULTS AND DISCUSSION

#### A. Structural properties under pressure

The  $\text{CoCr}_2\text{O}_4$  compound retains the cubic spinel structure up to 16 GPa (Fig. 2); both the lattice and interatomic parameters of the  $Fd-3m$  phase could be obtained up to that pressure (Figs. 3 and 4). Further compression leads to a reversible [54] asymmetric broadening for specific Bragg peaks [Fig. 2(b)]. Possible reasons behind this Bragg peak broadening might be nonhydrostatic conditions, cationic inversion, or a structural transition. Since we have employed helium as a PTM in our XRD experiment, we can most likely exclude any nonhydrostatic effects as the cause behind this effect.

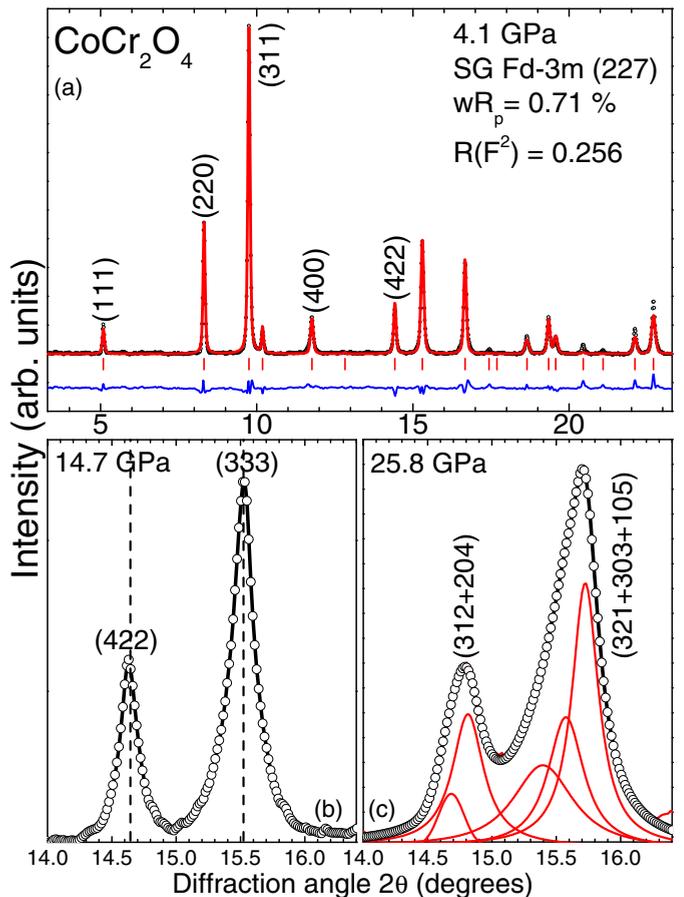


FIG. 2. (Color online) (a) Example of a Rietveld refinement for the  $Fd-3m$  phase at 4.1 GPa. Dots correspond to the measured spectrum, whereas the red and blue solid lines represent the best refinement and the difference between the experimental and refined patterns, respectively. Vertical ticks mark the Bragg peak positions. Expanded views of the (422) and (333)  $Fd-3m$  Bragg peaks before [(b) at 14.7 GPa] and after [(c) at 25.8 GPa] the cubic-tetragonal transition are also displayed.

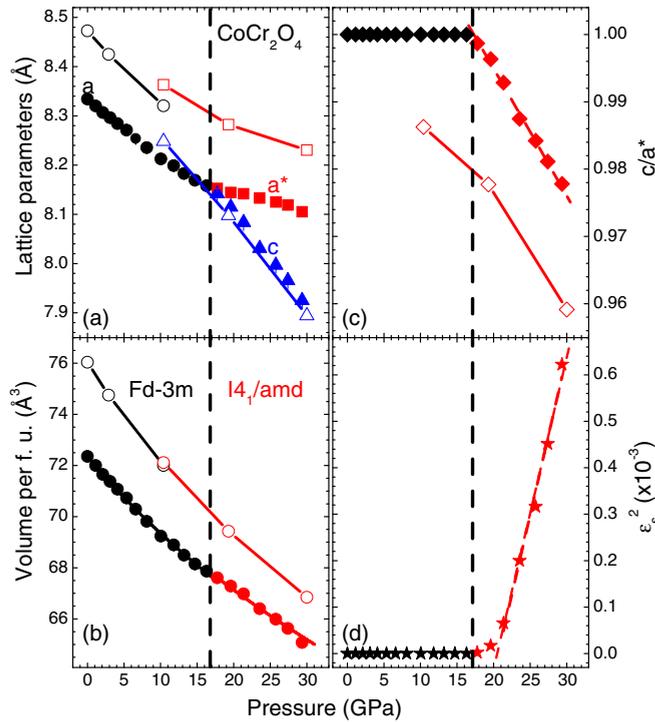


FIG. 3. (Color online) The evolution of (a) the lattice parameters, (b) the unit cell volume per formula unit, and (c) the axial ratio as functions of pressure for both the *Fd-3m* and tetragonal phases of CoCr<sub>2</sub>O<sub>4</sub>. The vertical dashed lines mark the onset of the (experimental) structural transition, whereas the open symbols represent the calculated structural parameters with DFT (black for the *Fd-3m* paramagnetic and red for the *I4<sub>1</sub>/amd* ferrimagnetic phase, respectively). Notice that we employ the pseudocubic  $a^* (=a_{\text{tet}}\sqrt{2})$  lattice constant for direct comparison. (d) Plot of the square of the symmetry-breaking tetragonal strain  $\epsilon_s^2 \approx [(c - a^*)/a_{\text{cub}}]^2$  against pressure, where  $a^*$  and  $c$  are the lattice parameters of the tetragonal phase, and  $a_{\text{cub}}$  is the lattice parameter of the cubic phase extrapolated into the stability field of the tetragonal phase. The dashed red line represents the linear fit expected from Landau theory.

As for the possibility of a pressure-induced (partial) cationic inversion, i.e., mutual cationic exchange in the tetrahedral and octahedral spinel sites, it is quite frequent for spinels under pressure [55,56]. In order to check this inversion scenario, we have compared the ambient-pressure cubic lattice parameter  $a$  and that of the fully decompressed sample [54]; such direct comparison can provide insight into any structural damage or disorder suffered by the material upon compression [56,57]. Since the  $a$  values of the starting and the decompressed samples are very close, we can safely exclude any permanent disorder taking place in CoCr<sub>2</sub>O<sub>4</sub>. On the other hand, a more local probe such as Raman spectroscopy is more suitable for identifying microstructural changes. Actually, the partial inversion of the spinel structure would result in the appearance of sidebands in the high-frequency stretching modes due to the different cationic sizes [58]. Since we could not detect such “new” modes in the Raman spectra of CoCr<sub>2</sub>O<sub>4</sub> near the transition pressure (Fig. 5), we exclude the possibility of a pressure-induced cationic inversion in CoCr<sub>2</sub>O<sub>4</sub>. Therefore,

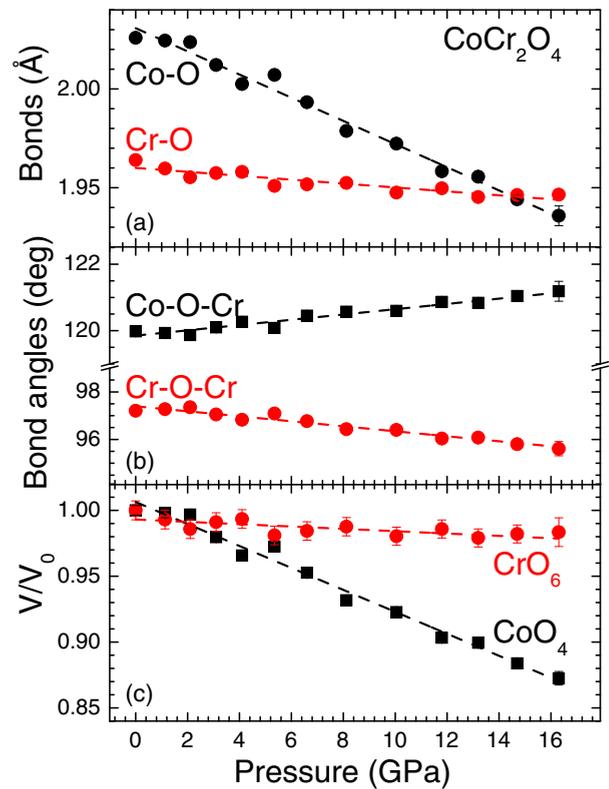


FIG. 4. (Color online) Pressure-induced variation of (a) the Co-O and Cr-O bond lengths and (b) the Cr-O-Cr and Co-O-Cr bond angles for the *Fd-3m* phase of CoCr<sub>2</sub>O<sub>4</sub>. The error bars lie within the symbols. (c) The normalized polyhedral volume is also plotted as a function of pressure.

we attribute this pressure-induced asymmetric Bragg peak broadening above 16 GPa to a structural transition.

The observed high-pressure phase could be assigned to a tetragonal distortion of the original cubic structure. Due to the broadening of the Bragg peaks after the cubic-tetragonal transition, which arises partly from the aforementioned peak splittings, only the lattice parameters could be extracted for the high-pressure phase. For the same reason, we could not assign a unique space group for the high-pressure phase; nevertheless, and by taking into account the structural behavior of similar Cr-based spinels under pressure [11,12], we have employed the tetragonal SG *I4<sub>1</sub>/amd* ( $Z = 4$ ) for our refinements. The high-pressure *I4<sub>1</sub>/amd* phase can be easily derived from the starting *Fd-3m* structure: the  $c$  axis in the two structures is common, whereas the  $a_{\text{tet}}$  axis equals the cubic lattice parameter  $a_{\text{cub}}$  divided by  $\sqrt{2}$ .

The lattice parameters obtained for both phases are plotted in Fig. 3(a). We employ the pseudocubic  $a^* = a_{\text{tet}}\sqrt{2}$  tetragonal lattice constant for direct comparison. The  $a^*$  axis does not show any visible change at the transition point, whereas the  $c$  axis contracts by  $\sim 0.13\%$  with respect to the *Fd-3m* lattice parameter [Fig. 3(a)]. From the experimental  $P$ - $V$  data alone, however, it is difficult to determine whether there is any volume discontinuity at the transition point [Fig. 3(b)]. Since the cubic-tetragonal transition in CoCr<sub>2</sub>O<sub>4</sub> is expected to be of second order from space-group symmetry considerations

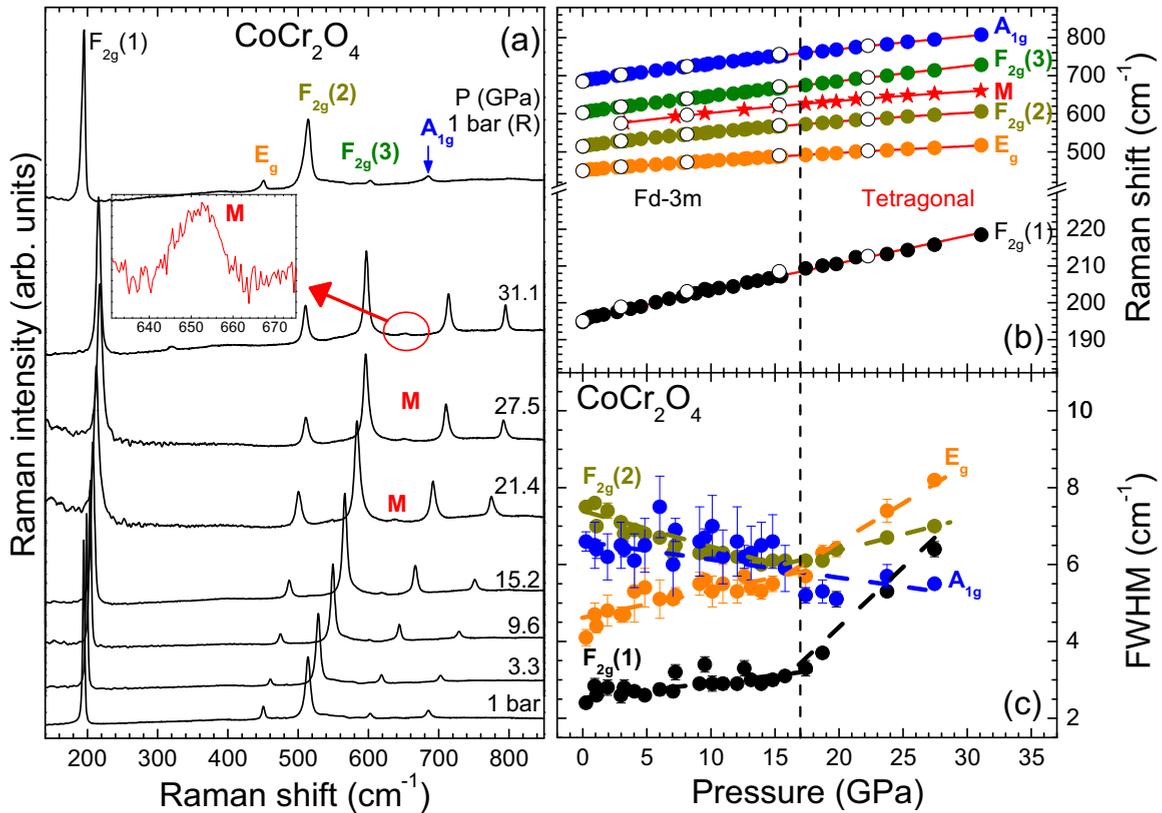


FIG. 5. (Color online) (a) Selected Raman spectra of  $\text{CoCr}_2\text{O}_4$  at various pressures ( $\lambda = 532 \text{ nm}$ ,  $T = 300 \text{ K}$ ). The assignment of each mode is provided. (b) Raman mode frequencies and (c) selected full widths at half maximum (FWHMs) as functions of pressure. Closed and open circles depict measurements upon increasing and decreasing pressure.

[59], the Landau theory of phase transitions can be used for verification [60,61]. For this reason, we plot the square of the tetragonal strain  $\varepsilon_S$  against pressure in Fig. 3(d); since the relationship between these two parameters is not linear, we classify the cubic-tetragonal transition as a *first-order structural transition*.

Further compression of the high-pressure tetragonal phase leads to a continuous decrease for both the  $a^*$  and  $c$  axes, with the  $c$  axis being more compressible throughout the investigated pressure range [Fig. 3(a)]. This variation in the axial pressure dependence is clearly captured via the continuous decrease of the tetragonal  $c/a^*$  axial ratio up to 30 GPa [Fig. 3(b)].

Regarding the  $P$ - $V$  data of the cubic and tetragonal phases, we have fitted each phase with a separate BM EOS function [30] [Fig. 3(c)]. The derived elastic parameters are  $V_0/Z = 72.4 \text{ \AA}^3$  (as measured),  $B_0 = 209(\pm 8) \text{ GPa}$ , and  $B'_0 = 5(\pm 1)$  for the cubic phase, and  $V_{\text{Tr}}/Z = 67.6 \text{ \AA}^3$  (as measured),  $B_{\text{Tr}} = 313(\pm 8) \text{ GPa}$ , and  $B'_{\text{Tr}} = 4$  (fixed) for the tetragonal phase at the transition pressure point  $P_{\text{Tr}} = 17.8 \text{ GPa}$ . The bulk modulus  $B_0$  of the cubic  $\text{CoCr}_2\text{O}_4$  phase is consistent with the bulk moduli reported for other Cr-based oxospinel [54].

Turning finally to the interatomic parameter evolution against pressure for the  $Fd-3m$  phase, we display the two different metal-oxygen bond lengths and the interatomic bond angles as a function of pressure in Figs. 4(a) and 4(b). The longer Co-O bond distance decreases much faster compared to the Cr-O bond, which is almost incompressible [Fig. 4(a)].

This is also evidenced by the significant pressure-induced relative volume change of the two different  $\text{CoO}_4$  and  $\text{CrO}_6$  polyhedral units comprising the spinel structure [Fig. 4(c)]. The two bond lengths become equivalent near 15 GPa, just before the tetragonal distortion. On the contrary, the two interatomic Co-O-Cr and Cr-O-Cr bond angles are almost pressure insensitive [Fig. 4(b)]. This bond angle resilience against pressure appears to be a common feature among Cr-based spinels [11,12].

## B. High-pressure Raman investigation

In order to probe the lattice dynamics of  $\text{CoCr}_2\text{O}_4$ , we have employed high-pressure Raman spectroscopy. The results are displayed in Fig. 5. For the starting  $Fd-3m$  phase, we can detect all five of the expected Raman-active modes [62,63] (Table I). The  $Fd-3m$  Raman modes exhibit normal behavior upon pressure increase, i.e., their frequencies increase under compression [Fig. 5(b) and Table I]. The effect is more pronounced for the  $F_{2g}(2)$ ,  $F_{2g}(3)$ , and  $A_{1g}$  modes assigned to stretching vibrations [63], since the respective bond lengths are more compressible than the bond angles [Figs. 4(a) and 4(b)].

Except from the Raman-active modes of the  $Fd-3m$  phase, a low-intensity band (termed  $M$ ) located at  $\sim 580 \text{ cm}^{-1}$  could be resolved near 5 GPa (Fig. 5 and Table I). Careful inspection of the Raman spectra indicates that this band resides at the base of the much more intense  $F_{2g}(2)$  mode at ambient conditions, and is gradually separated upon compression. Given its

TABLE I. Assignment [62,63], frequencies, pressure coefficients, and the mode Gruneisen parameters  $\gamma$  of the Raman modes of  $\text{CoCr}_2\text{O}_4$ . The pressure dependence of the Raman-active modes is described by the relation:  $\omega(P) = \omega_0 + \alpha P + bP^2$  [2], where frequency  $\omega_0$  is in  $\text{cm}^{-1}$  and pressure  $P$  in GPa. The Gruneisen parameters  $\gamma$  are determined from the relation  $\gamma = (B_0/\omega_0)(\partial\omega/\partial P)$ , where  $B_0 = 209$  GPa (this work).

Mode	$\omega_{\text{Tr}}$ ( $\text{cm}^{-1}$ )	$\partial\omega/\partial P$ ( $\text{cm}^{-1}/\text{GPa}$ )	$\partial^2\omega/\partial P^2$ ( $\text{cm}^{-1}/\text{GPa}^2$ )	$\gamma$
$F_{2g}(1)$	195.7(1)	0.75		0.8
$E_g$	452.2(2)	2.6	-0.02	1.2
$F_{2g}(2)$	516.2(3)	3.8	-0.03	1.54
$F_{2g}(3)$	605.8(3)	4		1.38
$A_{1g}$	687.6(3)	4.6	-0.03	1.4
$M$	563.2(9)	4.3(1)	-0.04	

“unexpected” presence and extremely low relative intensity compared to the spinel Raman-active bands, we attribute this  $M$  mode to a local defect or impurity of crystalline  $\text{CoCr}_2\text{O}_4$ . Actually, both the extrapolated ambient-pressure frequency and the pressure dependence of the  $M$  band coincide with the  $A_{1g}$  mode of  $\text{Cr}_2\text{O}_3$  [64] (Table I). Hence, our assignment for this extra  $M$  mode as a local defect or impurity band appears reasonable.

As for the high-pressure tetragonal  $I4_1/amd$  phase, ten Raman-active modes are expected [65]. In our case, however, we could not observe either any new Raman-active modes (something which excludes the pressure-induced cationic inversion scenario as already discussed [58]), or subtle or abrupt frequency shifts of the measured Raman modes in the vicinity of the transition point [Fig. 5(b) and Table I]. Even though the clear distinction between the  $Fd-3m$  and  $I4_1/amd$  phases is not always possible from Raman spectroscopy (e.g., the tetragonally distorted  $\text{NiCr}_2\text{O}_4$  spinel does not show the Raman features expected for the  $I4_1/amd$  phase [66]), a more thorough analysis of the measured Raman bands reveals delicate changes near the cubic-tetragonal transition.

In particular, the widths of the  $F_{2g}(1)$  and  $E_g$  modes tend to increase beyond  $\sim 17$  GPa [Fig. 5(c)]. Since (a) we have employed He as PTM and (b) we do not observe similar behavior (broadening) in the widths of the remaining Raman modes [the width of the  $A_{1g}$  mode exhibits an almost linear decrease under pressure, Fig. 5(c)], we can safely exclude any extrinsic effects such as nonhydrostaticity as the reason behind these width modifications. On the contrary, we assign these pressure-induced peak broadenings to the tendency of the respective Raman modes to split above that pressure. Given that the tetragonal distortion of the cubic structure is small (Fig. 3), the detection of these Raman peak splittings is probably hindered by the resolution of the spectrometer ( $\sim 2$   $\text{cm}^{-1}$ ). Hence, the pressure-induced peak broadenings for specific Raman-active modes can serve as an indirect probe for the structural distortion of the spinel phase above 17 GPa, in excellent agreement with our XRD study.

We should finally mention that the integrated intensities of the  $E_g$  and  $F_{2g}(3)$  modes exhibit substantial increase after the cubic-tetragonal transition [54]. This Raman intensity enhancement can most likely be attributed to resonance effects

coming into play after the structural distortion, since (a) both the  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  intra- $d-d$  electronic excitations lie just below the incident laser energy ( $E_{\text{laser}} = 2.3$  eV) at ambient conditions [22], and (b) both of these  $d-d$  transitions are expected to shift towards higher energies upon compression [14], thus satisfying resonance Raman conditions beyond a certain pressure.

### C. Calculated magnetic properties

We have additionally conducted *ab initio* calculations for understanding the effect of pressure on the magnetic properties of  $\text{CoCr}_2\text{O}_4$  under pressure. Comparison between the experimental and calculated structural parameters [54] shows that the lattice parameter  $a$  for both the cubic and tetragonal phases of  $\text{CoCr}_2\text{O}_4$  is overestimated [Fig. 3(a)]. Nevertheless, the trends between the calculated and experimental structural parameters under pressure are in very good agreement [Figs. 3(a)–3(c)].

In Fig. 6 we plot the axial ratio  $c/a^*$  dependence against pressure assuming different magnetic configurations for  $\text{CoCr}_2\text{O}_4$ . The FerroM phase (black circles) stands for all  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  spin up (or all spin down). The FerriM phases (colored symbols) stand for half  $\text{Cr}^{3+}$  spin up in the same plane on the  $c$  axis and the other half  $\text{Cr}^{3+}$  spin down, with all  $\text{Co}^{2+}$  spin up (or all spin down). The energy surface shows a single minimum point when manually varying the  $c/a^*$  axial ratio at a high pressure value [54], confirming the results from the relaxation. It is clear that the ferrimagnetic state *always* favors a  $c/a^* < 1$ , i.e. a tetragonal structure; application of external pressure leads to the enhancement of the tetragonal distortion. Interestingly, a tetragonal deviation from the cubic symmetry is suspected for  $\text{CoCr}_2\text{O}_4$  upon entering the ferrimagnetic state below  $\sim 96$  K, even though such a transition has not been observed directly [21].

Furthermore, we have also checked the possibility of an orthorhombic distortion instead of a tetragonal one for the ferrimagnetic state, another possible structural modification observed in Cr spinels upon magnetic ordering [67]. In order

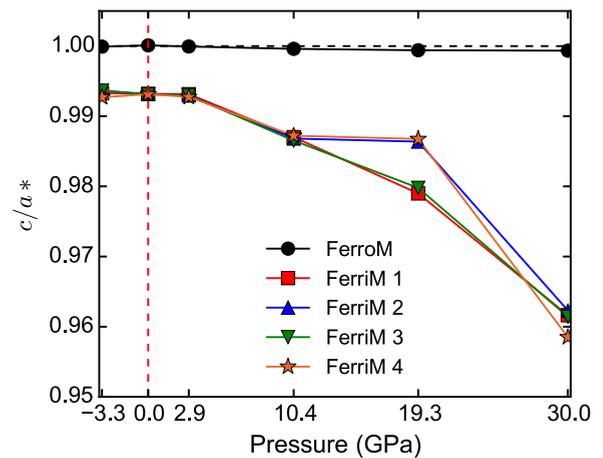


FIG. 6. (Color online) The axial ratio  $c/a^*$  as a function of pressure for different magnetic configurations of  $\text{CoCr}_2\text{O}_4$ . FerroM stands for the ferromagnetic case, whereas FerriM stands for the ferrimagnetic cases with four equivalent ways to alter the  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  spins up and spins down (see text).

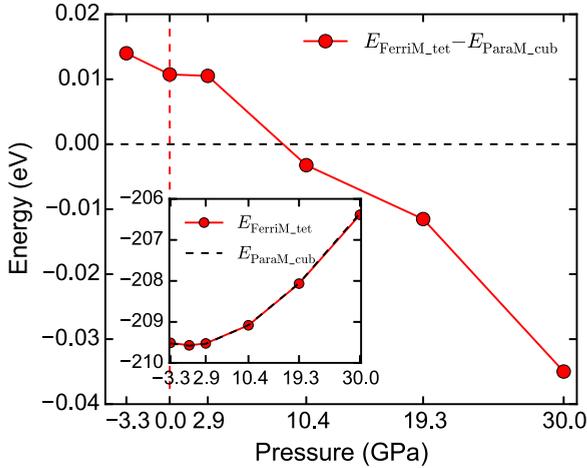


FIG. 7. (Color online) Energy difference between the paramagnetic cubic (ParaM\_cub) and the ferrimagnetic tetragonal (FerriM\_tet) phases of  $\text{CoCr}_2\text{O}_4$  as a function of pressure.

to achieve this, we relaxed the ferrimagnetic cell assuming an orthorhombic initial structure with slightly different  $a$ ,  $b$ , and  $c$  values and let them freely relax for each given volume. The resulting  $a/b$  ratio values deviate below 0.4% from 1 within the simulation range, i.e., from  $-3.3$  to  $30$  GPa. Since the calculated  $a/b$  values are very close to 1 ( $c/a^*$  is nearly the same as in the tetragonal cell), we conclude that the ferrimagnetic configuration is accompanied by a tetragonal distortion.

In Fig. 7 we display the energy difference between the paramagnetic cubic and the ferrimagnetic tetragonal phases of  $\text{CoCr}_2\text{O}_4$  as a function of pressure. We can observe a crossing between the two phases close to 10 GPa, indicating that higher pressure favors the ferrimagnetic tetragonal ground state. In order to gain further insight into the magnetic properties, we have extracted the values of the magnetic exchange interactions  $J_{AA}$ ,  $J_{BB}$ , and  $J_{AB}$  assuming a cubic structure at different pressures (Table II), and by employing the Heisenberg model of Ref. [68]. The calculated  $J_{AA}$ ,  $J_{AB}$ , and  $J_{BB}$  values at 0 GPa ( $U_{A(\text{Co})} = 3.3$  eV,  $U_{B(\text{Cr})} = 3.7$  eV) are in very good agreement with previous results obtained from the local spin density approximation (LSDA) +  $U$  [68]. Compression leads to the strengthening of all  $J$  interactions, a direct result from the shrinkage of the lattice. According to the theory developed by Lyons, Kaplan, Dwight, and Menyuk (LKDM)

TABLE II. Calculated magnetic exchange interactions assuming a cubic structure for all four constructed magnetic configurations at various pressures by employing the Heisenberg model of Ref. [68] (here  $U_{A(\text{Co})} = 3.3$  eV,  $U_{B(\text{Cr})} = 3.7$  eV). The term  $A$  stands for the base energy without the addition of the magnetic contribution.

$P$ (GPa)	$V(\text{\AA}^3)$	$A$ (eV)	$J_{AA}$ (meV)	$J_{AB}$ (meV)	$J_{BB}$ (meV)
-3.3	310.00	-209.497	-0.84	-8.11	-2.10
0	304.00	-209.555	-0.92	-9.00	-2.97
2.9	299.00	-209.500	-1.00	-9.83	-3.37
10.4	288.00	-209.041	-1.20	-11.95	-4.86
19.3	277.00	-208.003	-1.47	-14.58	-6.71
30	266.00	-206.292	-1.82	-17.86	-8.93

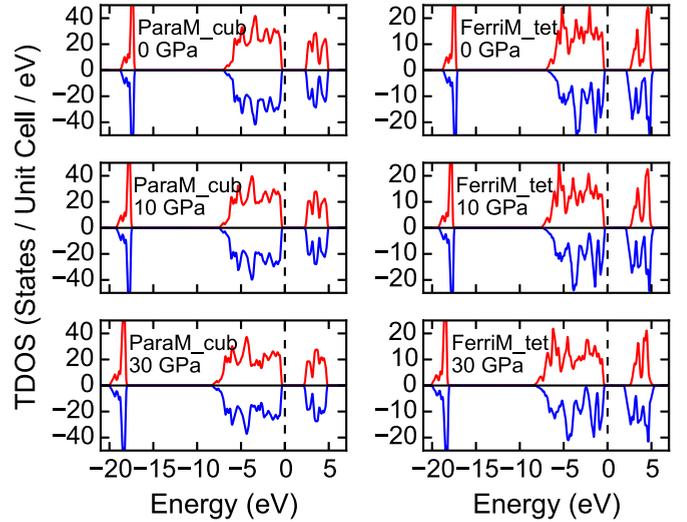


FIG. 8. (Color online) Spin-resolved total density of states (TDOS) of the paramagnetic cubic (ParaM\_cub) and the ferrimagnetic tetragonal (FerriM\_tet) phases at various pressures. The red and blue lines correspond to spin-up and spin-down states, respectively. Notice that for the ParaM\_cub phase, the spin-up and spin-down states are identical.

[69], the magnetic ground state and/or the magnetic frustration of a spinel compound can be described by the parameter  $u \approx J_{BB}/J_{AB}$ . In particular, the larger the magnitude of  $u$ , the more frustrated is the respective spinel. Given that the  $J_{BB}$  coupling constant displays a larger enhancement under pressure compared to  $J_{AB}$  (Table II), we can reasonably anticipate the enhancement of the magnetic frustration in  $\text{CoCr}_2\text{O}_4$  under compression. Such a hypothesis is consistent with experimental high-pressure magnetization studies [23–25].

In order to look for any electronic effects taking place near the magnetostructural transition, we have calculated the spin-resolved total density of states for the two magnetic and structural configurations of  $\text{CoCr}_2\text{O}_4$  at three different pressures: 0 GPa, 10 GPa (close to the calculated transition point), and 30 GPa (Fig. 8). Application of external pressure induces the broadening of the electronic bands for both phases due to lattice shrinkage, which in turn leads to slightly smaller band gap values. In particular, the band gap of the paramagnetic cubic phase decreases from 2.77 to 2.64 eV. On the other hand, the band gap of the spin-up states for the ferrimagnetic tetragonal phase does not change under pressure (the 0 GPa value is 2.87 eV), whereas the band gap of the spin-down states drops from 2.55 to 2.40 eV. In addition, the Bader charge analysis for both the cubic and tetragonal phases does not show any considerable change throughout the examined pressure range [54]. Overall, the general shapes of the TDOS and Bader charge transfer do not change much upon compression, indicating that the pressure-induced cubic-tetragonal transition is not accompanied and/or induced by electronic charge effects.

#### D. Discussion

Systematic high-pressure structural investigations on oxide spinels have demonstrated that the starting  $Fd-3m$  phase transforms into the denser  $\text{CaFe}_2\text{O}_4^-$ ,  $\text{CaTi}_2\text{O}_4^-$ , or a  $\text{CaMn}_2\text{O}_4^-$

type structure upon sufficient compression [70,71]. Similar high-pressure studies on Cr-based oxospinels, however, appear to deviate somewhat from this established trend. In particular, a theoretical study proposed the decomposition of the  $\text{MgCr}_2\text{O}_4$ ,  $\text{MnCr}_2\text{O}_4$ , and  $\text{ZnCr}_2\text{O}_4$  spinels into their constituent oxides under pressure [72]. Subsequent experimental studies, however, on  $\text{ZnCr}_2\text{O}_4$  [73] and  $\text{MgCr}_2\text{O}_4$  [74] did not verify the decomposition scenario. In particular,  $\text{ZnCr}_2\text{O}_4$  undergoes a cubic-orthorhombic transition beyond 30 GPa [73], whereas  $\text{MgCr}_2\text{O}_4$  adopts a tetragonal  $I4_1/amd$  structure above 20 GPa ( $c/a^* = 0.8$  at the transition point) [74]; high-pressure structural data have not been reported for  $\text{MnCr}_2\text{O}_4$  up to now. On the other hand, pressure-induced decomposition was claimed to take place for the tetragonally distorted  $\text{NiCr}_2\text{O}_4$  spinel from Raman studies [66]. Furthermore, the  $\text{FeCr}_2\text{O}_4$  spinel transforms also into the  $I4_1/amd$  structure at 12 GPa ( $c/a^* \approx 1$  at the transition point) [75]. Finally,  $\text{CdCr}_2\text{O}_4$  adopts an orthorhombic  $\text{CaFe}_2\text{O}_4$ -type phase after combined high-pressure and high-temperature treatment [76]; a recent high-pressure infrared investigation indicated that a phase transition takes place above 15 GPa at room temperature as well [14]. Hence, the observed cubic-tetragonal distortion observed for  $\text{CoCr}_2\text{O}_4$  above 16 GPa complies with the structural trend of Cr-based oxospinels under pressure.

Turning now to the possible driving forces behind the observed pressure-induced structural distortion, these consist of underlying electronic (orbital and/or charge) [14,59,75,77] and/or magnetic [22,78] effects. Regarding the electronic part, we have already mentioned that our TDOS and Bader charge transfer calculations did not reveal any significant changes in the vicinity of the cubic-tetragonal transition. As for a possible pressure-induced orbital, i.e., Jahn-Teller effect in  $\text{CoCr}_2\text{O}_4$  as in isostructural  $\text{FeCr}_2\text{O}_4$  [75], we recall here that both  $\text{Co}^{2+}$  ( $3d^7 : e^4 t_2^3$ ) and  $\text{Cr}^{3+}$  ( $3d^3 : t_{2g}^3 e_g^0$ ) cations are orbitally inactive in the starting  $Fd-3m$  phase (Fig. 1). As a result, a plausible Jahn-Teller effect in this system would require or induce appreciable intercationic charge transfer in the vicinity of the cubic-tetragonal transition point, something which is also excluded by our Bader charge transfer calculations [54]. Therefore, we conclude that the magnetic component is the key ingredient behind the cubic-tetragonal transition in  $\text{CoCr}_2\text{O}_4$ .

By taking into account similar magnetoelastic transitions in Cr-based spinels [6,7,22], we *speculate* that the cubic-tetragonal transition is triggered by the enhancement of the magnetic frustration in  $\text{CoCr}_2\text{O}_4$ , resulting from the “disproportionate” strengthening of the various magnetic exchange interactions  $J_{AA}$ ,  $J_{BB}$ , and  $J_{AB}$  under pressure (Table II). This magnetic frustration is partially relieved by the lowering of the crystalline symmetry from cubic to tetragonal.

Finally, and given that ferroelectricity for  $\text{CoCr}_2\text{O}_4$  requires the magnetically frustrated state [3,18–21], we estimate that pressure will probably *enhance* the macroscopic electrical polarization. More appropriate experimental probes will be needed, however, in order to verify our assumptions.

#### IV. CONCLUSIONS

In summary, we have explored the structural, vibrational, magnetic, and electronic behavior of the multiferroic  $\text{CoCr}_2\text{O}_4$  spinel up to 30 GPa by a combination of experimental and *ab initio* methods. Our investigations reveal a reversible tetragonal distortion of the starting cubic structure above 16 GPa. Our DFT studies indicate that this structural modification is not accompanied by any appreciable electronic effects. On the other hand, our calculations indicate that the main driving force behind the observed structural transition in  $\text{CoCr}_2\text{O}_4$  is of magnetic origin, probably due to the disproportionate strengthening of the various magnetic exchange interactions.

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